Crystal Structure of Anhydrous Nitrates and Their Complexes. Part VII.[1] 1.5 Dinitrogen Tetroxide Solvate of Iron(III) Nitrate

By **Leslie J. Blackwell, Ernest K. Nunn,**† and **Stephen C. Wallwork,*** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Crystal structure determination has shown that this solvate exists in the form $[NO]^+{}_3[NO_3]^-[Fe(NO_3)_4]^-{}_2$ in which there is close association between the three $[NO]^+$ and the $[NO_3]^-$ ions to form a grouping $[N_4O_6]^{2+}$. The nitrogen atom of each $[NO]^+$ lies approximately along the bisector of each O–N–O angle of the nitrate ion with $ON^+\cdots O_2NO_2$ distances ranging from *ca.* 2.4 to 2.8 Å and the NO^+ axes tilted at angles ranging 10—51° out of the plane of the nitrate ion. The two crystallographically independent tetranitratoferrate(III) ions have the same trigonal dodecahedral structure as found in the tetraphenylarsonium salt with symmetrically bidentate nitrato-groups.

DINITROGEN tetroxide is a widely used oxidiser component in liquid bipropellant rocket engines. During the early testing of such engines a troublesome decrease in N_2O_4 flow rate was noted when the N_2O_4 which had been stored in stainless steel vessels was required to pass through small orifices such as needle valves and filters. This decay was found to be due to the deposition in the orifices of a brown material which was shown[2] by chemical analysis to be iron(III) nitrate solvated by N_2O_4, *i.e.* $Fe(NO_3)_3,xN_2O_4$ where x was said to vary from 1 to 9. The compound where $x = 1$ was first isolated[3] as a red-brown microcrystalline solid and the

---

† *Present address:* Department of Chemistry, Monash University, Wellington Road, Clayton, Victoria, Australia 3168.

[1] Part VI, J. Hilton, E. K. Nunn, and S. C. Wallwork, *J.C.S. Dalton*, 1972, 1973.

[2] Rocketdyne, 'Methods for Elimination of Corrosion Products of Nitrogen Tetroxide,' Final Report, Contract AFO4(611) 11620, July 1967.

[3] C. C. Addison, B. J. Hathaway, and N. Logan, *Proc. Chem. Soc.*, 1958, 51.

existence of compounds with $x > 1$ has been noted.[4] In one instance a solid of composition $Fe(NO_3)_3,1.5N_2O_4$ was isolated from the reaction of $Fe(CO)_5$ with liquid N_2O_4. A more recent vapour-pressure study[5] of the system $Fe(NO_3)_3,xN_2O_4$ gave clear evidence that the compound where $x = 1.5$ is of primary importance in this system as the stable species in the presence of liquid dinitrogen tetroxide and it was established that this material is the deposit responsible for flow decay of N_2O_4 through needle valves. The i.r. and Raman spectra of this 1 : 1.5 solvate suggested the presence of NO^+ ions as in the 1 : 1 solvate, which had been formulated as $[NO]^+[Fe(NO_3)_4]^-$, but it was not clear how the 1 : 1.5 solvate should be formulated. Moreover the NO^+ vibration was shifted to lower wavenumbers in the 1 : 1.5 solvate compared with the 1 : 1 solvate. Because of the great practical interest in this compound and the inability of chemical and other physical methods to provide a satisfactory formulation, it was decided to determine its crystal structure.

EXPERIMENTAL

The solvate was prepared by the reaction of $FeCl_3$ with N_2O_4 in the presence of ethyl acetate.[4] It was dissolved in ethyl acetate, filtered, and a large excess of dry N_2O_4 was added. Yellow plate-like crystals were deposited and these were used, after sealing into glass capillaries, in the first two *X*-ray diffractometer studies. In later preparations, it was found that if the plate-like crystals were filtered off and the mother liquor set aside overnight at -20 °C small block-shaped crystals, more suitable for accurate *X*-ray diffraction measurements, separated out. In view of the highly hygroscopic nature of the adduct the loading of crystals into the capillaries was carried out in a glove-box and the capillaries were temporarily sealed with grease until they were flame-sealed outside the glove-box.

Oscillation and Weissenberg *X*-ray photographs of the plate-like and of the block-shaped crystals confirmed that they were merely different growth forms of the same crystal structure. The space group was found to be $P2_1/c$ from the systematic absences. The first *X*-ray diffractometry study was carried out on a plate-like crystal of dimensions *ca.* $0.5 \times 0.3 \times 0.1$ mm sealed into a thin-walled glass capillary with its long dimension parallel to the capillary axis. This was mounted on a Hilger and Watts linear diffractometer so as to rotate about the long axis of the crystal which was the *a* crystallographic axis. The unit-cell dimensions were refined on the diffractometer and the values obtained were $a = 10.21(6)$, $b = 19.87(4)$, $c = 14.33(4)$ Å, $\beta = 128.3(3)°$. Significant intensities were measured for 1912 reflections on the layers $h = 0$—11. One of us was offered an opportunity to try out a Philips computer-controlled four-circle diffractometer at Eindhoven and the same crystal was used for this trial. The instrument was allowed to choose its own unit cell and it selected an alternative $P2_1/c$ cell of dimensions $a = 10.423$, $b = 19.917$, $c = 16.268$ Å, $\beta = 136.4°$. This cell has the same *a* and *b* axes as that previously chosen but the *c* axis is [201] of the previous cell. *Ca.* 2 000 intensities were measured in *ca.* 16 h by rapid θ—2θ scans and 1 220 of them proved to have intensities significantly above the background.

The early work on the structure was carried out during sabbatical leave of one of us (E. K. N.) with data collected on the linear diffractometer. Intensities were corrected for Lorentz and polarisation factors but not for absorption and a three-dimensional Patterson map was calculated from the F_o^2 values so obtained. The general position in $P2_1/c$ is four-fold but it was clear from the calculated volume of the unit cell that there must be eight of the formula units $Fe(NO_3)_3$, $1.5N_2O_4$ in the unit cell, and therefore two of these in the asymmetric unit. It was found to be possible to interpret all the strong peaks in the Patterson function in terms of the vectors between the symmetry-related positions of each of two crystallographically independent iron atoms and the cross-vectors between the two sets of positions. Structure factors were calculated for the iron atoms only in the positions so derived and a Fourier synthesis phased on these calculated structure factors revealed some planar triangular arrangements of peaks near each of the two iron atoms that could be interpreted as nitrato-groups co-ordinated to the iron atoms in a bidentate manner. From the arrangement of these triangular groups it was clear that each iron atom was present as a tetranitratoferrate ion with the same structure as that already found[5] in $[Ph_4As]^+[Fe(NO_3)_4]^-$ though some of the atoms were still missing. The nitrogen and oxygen atoms which had been located were included in the structure-factor calculation and the Fourier synthesis based on the revised phases showed most of the missing atoms in the tetranitratoferrate groups. Successive structure-factor and Fourier calculations revealed further atoms, but not all, in these groups and no sensible pattern could be recognised in the peaks which should represent the remaining atoms in the structure.

This point of difficulty coincided with the end of the period of sabbatical leave for E. K. N. who, after returning home, made further attempts to solve the structure with the data collected on the Philips diffractometer. Meanwhile a Hilger and Watts computer-controlled four-circle diffractometer became available to the other investigators remaining at Nottingham. It was felt that more accurate data could be collected on a new crystal over a longer counting period and that such data might reveal more clearly the remaining atoms in the structure. A block-shaped crystal of dimensions *ca.* $0.2 \times 0.2 \times 0.3$ mm was therefore sealed into a capillary tube, together with a drop of N_2O_4 to prevent decomposition, and mounted on this diffractometer. The reflections were indexed according to the same unit cell as had been used with the linear diffractometer data and the refined cell dimensions were found to be: $a = 10.419(4)$, $b = 19.930(10)$, $c = 14.435(5)$ Å, $\beta = 128.89(2)°$. Significant intensities were measured for 1 731 reflections having $\theta \leqslant 20°$ using a scintillation counter, a θ—2θ scan, and Mo-K_α radiation ($\lambda = 0.710\ 69$ Å). At a later stage in the structure analysis a further 1 199 significant reflections were measured in the same way for a slightly larger crystal and for $20° < \theta \leqslant 30°$. These were placed on a common scale with the previous reflections by measurements on a standard reflection and were merged with the other reflections to obtain a more accurate refinement.

Repetition of the three-dimensional Patterson synthesis confirmed the positions previously determined for the iron atoms. A Fourier synthesis phased on these two iron atoms again showed most, but not all, of the remaining atoms in the $Fe(NO_3)_4$ units. The rest were located quickly

---

[4] C. C. Addison, P. M. Boorman, and N. Logan, *J. Chem. Soc.*, 1965, 4978.

[5] T. J. King, N. Logan, A. Morris, and S. C. Wallwork, *Chem. Comm.*, 1971, 554.

by successive structure-factor and least-squares calculations alternating with difference-Fourier syntheses, and 10 further peaks for the remaining N_4O_6 atoms in the asymmetric unit were then found. These were in the form of a nitrate ion, $[NO_3]^-$, surrounded by three nitrosonium ions, $[NO]^+$, in fairly close contact so that the whole group may be regarded [6] as a single cation $[N_4O_6]^{2+}$. By the time the whole structure had been revealed in this way the parallel attempt to solve the structure from the Philips data had located all the atoms of the two tetranitratoferrate groups and, with the information about the nature of the rest of the structure, the atoms of the $[N_4O_6]^{2+}$ cation were immediately recognisable.

Independent refinements of the structure by least-squares methods were then carried out using each of the three sets of data. The data from the linear diffractometer and from the Philips diffractometer were regarded as being less accurate (and they were also less numerous) so the refinements based on these were only taken as far as convergence with isotropic temperature factors for most N and O atoms, and anisotropic thermal parameters for Fe and the $[N_4O_6]^{2+}$ group, apart from the central N atom. In both these refinements the weighting scheme used was $w = 1/(\sin\theta/\lambda)$ and during the refinement with the linear diffractometer data 96 weak reflections were eliminated, since they showed poor agreement between F_o and F_c, leaving 1 816 reflections. The final R in this case was 0.075. In the case of the Philips data all 1 220 reflections were retained throughout and the final R was 0.063. In the refinement based on the data from the Hilger and Watts four-circle diffractometer all the atoms were eventually assumed to have anisotropic thermal parameters, 2 930 reflections were used, except for two with large $w\Delta F$ omitted in the last few cycles, and the weighting scheme was $w = 1$ if $F_o \leqslant A$, otherwise $w = (A/F_o)^2$, with $A = 30$ and F_o on the absolute scale. The final R value was 0.039. In all the refinements it was assumed that each $[NO]^+$ group would have nitrogen as the more positive end lying nearest to the $[NO_3]^-$ group. An attempt to test this assumption was made towards the end of the refinement with the Hilger and Watts four-circle diffractometer data by exchanging the co-ordinates of the N and O atoms in the three $[NO]^+$ groups. As expected, the temperature factors of the atoms which had originally been treated as oxygen decreased and those of atoms originally treated as nitrogen increased, thereby making the thermal parameters more unequal. There was also a slight increase in R. While not being regarded as conclusive, this test seems to indicate that the original assignment of the atomic positions was correct.

TABLE 1

Dimensions of the $[N_4O_6]^{2+}$ ion

	(1)*	(2)	(3)
(*a*) Interatomic distances (Å)			
N(9)–O(25)	1.24(1)	1.29(4)	1.25(6)
N(9)–O(26)	1.21(1)	1.20(7)	1.14(5)
N(9)–O(27)	1.24(1)	1.24(5)	1.23(4)
N(10)–O(28)	0.90(3)	1.02(7)	1.02(7)
N(11)–O(29)	0.90(1)	0.96(5)	0.92(4)
N(12)–O(30)	0.99(1)	0.98(4)	0.98(4)
N(10) · · · O(25)	2.41(1)	2.38(6)	2.42(3)
N(10) · · · O(26)	2.78(2)	2.66(4)	2.67(5)
N(11) · · · O(26)	2.72(2)	2.75(4)	2.65(6)
N(11) · · · O(27)	2.67(2)	2.64(6)	2.54(6)
N(12) · · · O(25)	2.44(1)	2.46(6)	2.37(4)
N(12) · · · O(27)	2.56(1)	2.61(6)	2.51(6)
O(29) · · · O(27)	2.56(2)	2.60(5)	2.53(6)
(*b*) Angles (°)			
O(25)–N(9)–O(26)	120(1)	116(3)	119(4)
O(26)–N(9)–O(27)	124(1)	130(3)	128(5)
O(27)–N(9)–O(25)	116(1)	114(4)	113(4)
N(9)–O(25)–N(10)	103(1)	101(3)	99(2)
N(9)–O(26)–N(10)	86(1)	90(2)	89(3)
N(9)–O(26)–N(11)	94(1)	88(2)	90(3)
N(9)–O(27)–N(11)	95(1)	93(3)	94(3)
N(9)–O(27)–N(12)	93(1)	95(3)	94(3)
N(9)–O(25)–N(12)	99(1)	101(3)	101(2)
O(25)–N(10)–O(26)	48(1)	49(1)	47(1)
O(26)–N(11)–O(27)	47(1)	48(1)	48(1)
O(27)–N(12)–O(25)	50(1)	49(1)	50(1)
O(25)–N(10)–O(28)	97(1)	96(5)	95(3)
O(26)–N(10)–O(28)	116(1)	123(4)	121(3)
O(26)–N(11)–O(29)	119(1)	124(4)	125(4)
O(27)–N(11)–O(29)	73(1)	77(4)	79(4)
O(27)–N(12)–O(30)	116(1)	116(5)	115(4)
O(25)–N(12)–O(30)	102(1)	103(4)	103(2)
O(27)–O(29)–N(11)	87(2)	82(3)	80(4)
N(9)–O(27)–O(29)	115(1)	113(3)	114(3)
(*c*) Distances (Å) out of the nitrate plane			
N(10)	0.91(2)	0.79(4)	0.93(4)
O(28)	0.27(1)	0.16(5)	0.33(3)
N(11)	0.11(1)	0.09(5)	0.01(4)
O(29)	0.27(1)	0.33(4)	0.27(3)
N(12)	−0.56(1)	−0.56(4)	−0.62(3)
O(30)	0.21(1)	0.21(3)	0.13(3)

* From refinements based on (1) the Hilger and Watts four-circle diffractometer data, (2) the Philips four-circle diffractometer data, and (3) the Hilger and Watts linear diffractometer data.

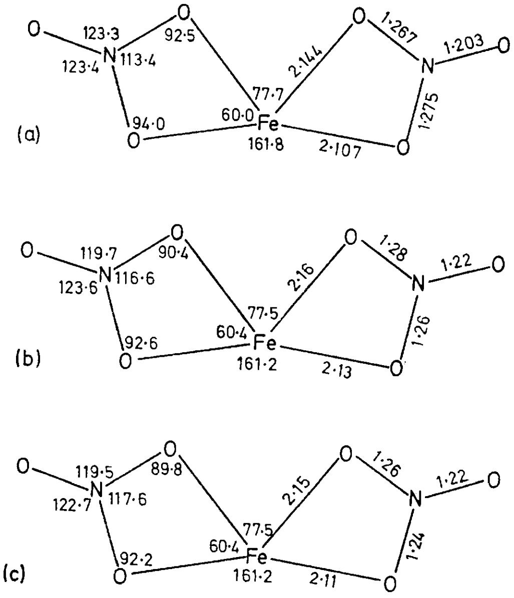

FIGURE 1 The averaged dimensions for the tetranitratoferrate ions; (a)—(c) denote refinements (1)—(3) defined in Table 1

Final atomic co-ordinates and thermal parameters, and comparisons of observed and final calculated structure factors, are given for all three refinements in Supplementary Publication No. SUP 21361 (14 pp., 1 microfiche),* together with detailed bond lengths and angles for the tetranitratoferrate ions corresponding to each set of final co-ordinates.

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[6] C. C. Addison, L. J. Blackwell, B. Harrison, D. H. Jones, N. Logan, E. K. Nunn, and S. C. Wallwork, *J.C.S. Chem. Comm.*, 1973, 347.

The averaged dimensions for the tetranitratoferrate groups are shown in Figure 1 and the dimensions for the $[N_4O_6]^{2+}$ cation, illustrated in Figure 2, are given in Table 1.

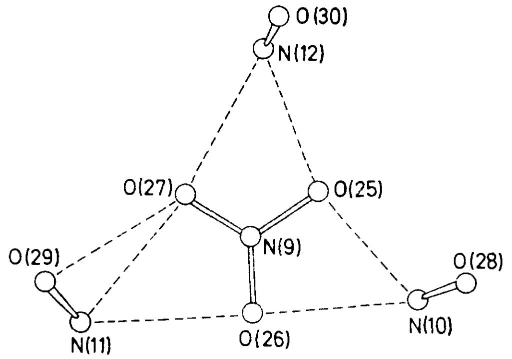

FIGURE 2 The $[N_4O_6]^{2+}$ cation

DISCUSSION

Before this work no metal nitrate–dinitrogen tetroxide solvate had had its crystal structure determined. It was not necessary to make any assumptions about the nature of the chemical species present in deriving the structure and the results show that there is no molecular N_2O_4 in the crystal lattice. Instead there are tetranitratoferrate ions and a previously unobserved grouping of a nitrate ion closely associated with three nitrosonium ions in what may be regarded[6] as a $[N_4O_6]^{2+}$ cation. The compound can therefore be formulated $[N_4O_6]^{2+}[Fe(NO_3)_4]^-_2$ or $[NO]^+_3[NO_3]^-[Fe(NO_3)_4]^-_2$. The structure is illustrated in Figure 3. It consists of zig-zag lines of tetranitratoferrate ions whose general direction is parallel to *b*. There are two of each of the two crystallographically independent $[Fe(NO_3)_4]^-$ ions in each repeat distance of the zig-zag along *b* and two such lines of these ions in each unit cell, at approximately *c*/4 and 3*c*/4, the plane of each zig-zag being approximately parallel to ($\bar{1}04$). In the angle of each zig-zag lies a $[N_4O_6]^{2+}$ unit with its mean plane *ca.* 60° from the *b* axis and approximately parallel to the *c* axis.

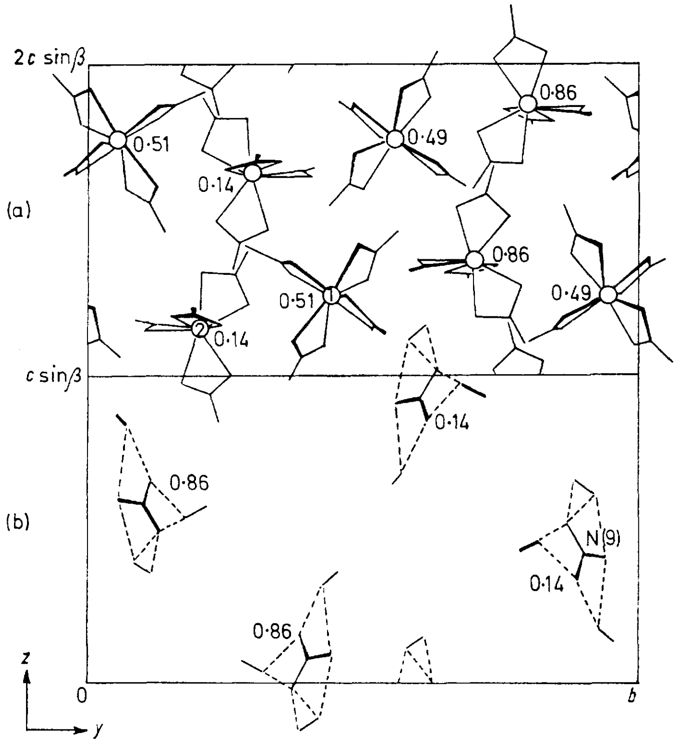

FIGURE 3 The structure projected along the *x* axis showing the *x* co-ordinate of the central atom of each group. (*a*) Tetranitroferrate ions, and (b) the $[N_4O_6]^{2+}$ cations

TABLE 2

Angles (°) between planes and lines, and mean deviations (Å) of atoms from these; (1)—(3) denote data from the three refinements (see Table 1 footnote)

(*a*) Deviations

Plane	Atoms	σ/Å × 10^4 (1)	(2)	(3)
(*A*)	O(1)—(3), N(1)	57	90	66
(*B*)	O(4)—(6), N(2)	6	45	126
(*C*)	O(7)—(9), N(3)	17	144	9
(*D*)	O(10)—(12), N(4)	9	8	99
(*E*)	O(13)—(15), N(5)	1	40	114
(*F*)	O(16)—(18), N(6)	44	233	250
(*G*)	O(19)—(21), N(7)	18	4	111
(*H*)	O(22)—(24), N(8)	19	172	83
(*I*)	O(25)—(27), N(9)	52	65	188

(*b*) Angles	(1)	(2)	(3)
(*A*)–(*B*)	71.8	72.4	71.9
(*A*)–(*C*)	82.7	83.2	83.4
(*A*)–(*D*)	8.5	8.0	8.9
(*B*)–(*C*)	14.5	15.1	15.5
(*B*)–(*D*)	80.1	80.3	80.8
(*C*)–(*D*)	89.4	89.0	87.8
(*E*)–(*F*)	85.0	84.3	84.6
(*E*)–(*G*)	3.2	3.1	3.4
(*E*)–(*H*)	79.7	80.8	80.8
(*F*)–(*G*)	87.4	87.0	87.4
(*F*)–(*H*)	16.2	15.8	15.4
(*G*)–(*H*)	77.5	78.4	78.2

(*c*) Angles to plane (I) from lines

Line	(1)	(2)	(3)
O(28)–N(10)	45.3	38.3	36.5
O(29)–N(11)	10.1	14.7	16.3
O(30)–N(12)	50.8	51.4	50.2

The dimensions of this unit have only been approximately established, as may be seen by the variation between the different determinations shown in Table 1. In particular the $[NO]^+$ distances are all shorter than the value (1.0619 Å) found[7] spectroscopically for the equilibrium internuclear distance in the gas phase and this may be due to thermal libration or to incomplete resolution of the pairs of atoms. Similar short distances have been found[8,9] in other *X*-ray determinations. The nitrogen atom of each $[NO]^+$ lies approximately on the bisector of each O–N–O angle of the nitrate ion and the N···O distances between the $[NO]^+$ and the nitrate ion are shorter the longer is the corresponding N–O bond length in the nitrate ion. This is consistent with either a varying small degree of covalent character in the N···O contacts or with an unequal distribution of the

---

[7] E. Miescher, *Helv. Phys. Acta*, 1956, **29**, 135.

[8] T. Höhle and F. C. Mijlhoff, *Rec. Trav. chim.*, 1967, **86**, 1153.

[9] B. A. Coyle, J. H. Holloway, S. W. Peterson, and J. M. Williams, *Science*, 1971, 173.

negative charge among the N–O bonds in $[NO_3]^-$ causing varying degrees of electrostatic attraction to the $[NO]^+$ ions. The longest N ••• O contact distances are of about the same order of size as the sum of the van der Waals radii for nitrogen and oxygen. The nitrate ion is planar, and the distances of the $[NO]^+$ atoms out of this plane are shown in Table 1 and the angles which the $[NO]^+$ axes make with it are given in Table 2. The differences shown by the three $[NO]^+$ groups are presumably due to packing effects.

The tetranitratoferrate ions have the nitrato-groups arranged in a symmetrically bidentate manner such that the co-ordinated oxygen atoms lie at the corners of a trigonal dodecahedron, as is commonly found with tetranitrato-species.[10] This results in the nitrogen atoms adopting a flattened tetrahedral arrangement round the central iron atom with N ••• Fe ••• N angles ranging from 135 to 138°. Each of the nitrato-groups is planar, but the planes are not quite directed at the iron atoms since these deviate from the planes of the nitrato-groups by distances ranging from 0.01 to 0.19 Å. Opposite pairs of nitrato-groups (Figure 1) are approximately coplanar and the pair above the equatorial square of oxygen atoms is approximately perpendicular to the pair below the equatorial square, so the ion has roughly D_{2d} symmetry. The averaged dimensions agree well with those already found [5] for this ion in the tetraphenylarsonium salt.

The closest contact distances between $[Fe(NO_3)_4]^-$ ions are O ••• O 3.058, and O ••• N 3.082 and 3.098 Å, all between the two crystallographically independent ions. There is also a close contact (O ••• O 2.772 Å) between the $[N_4O_6]^{2+}$ cation and one of the $[Fe(NO_3)_4]^-$ ions.

This work was sponsored in part by the U.S. Air Force Rocket Propulsion Laboratory through the European office of Aerospace Research, OAR, U.S. Air Force. We thank Professor C. C. Addison and the Department of Chemistry of Nottingham University for hospitality to E. K. N. during a sabbatical year, the S.R.C. for provision of the Hilger and Watts linear and four-circle diffractometers, Philips for the use of their four-circle diffractometer, the Director of the Cripps Computing Centre of Nottingham University for computing facilities, Professor T. J. King for assistance with the diffractometry and the computing, and Professor C. C. Addison and Dr. N. Logan for suggesting this research and for continued interest and encouragement.

[4/2693 *Received*, 23*rd December*, 1974]

[10] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.